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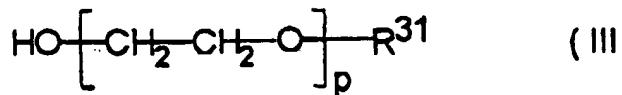
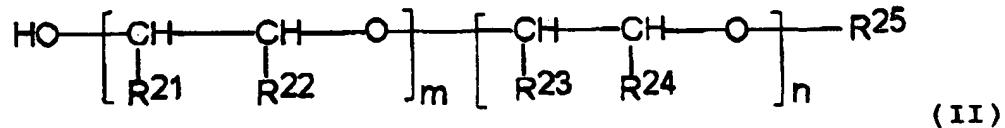
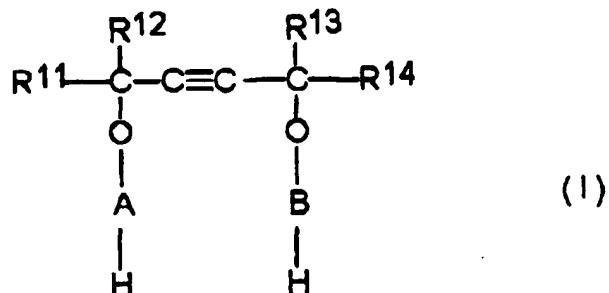
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(54) Ink jet recording ink

(57) An ink for ink jet recording and an ink jet recording method are provided which can realize a print having high color density and, even on recycled paper, a print having no significant feathering. The ink for ink jet recording comprises a water-soluble colorant, a water-soluble organic solvent, water, and a compound represented by the following formula (I), (II), or (III):



Description**BACKGROUND OF THE INVENTION****5 Field of the Invention**

The present invention relates to an ink for ink jet recording and an ink jet recording method which can produce a high-quality printed image on various recording media, for example, plain papers, recycled papers, and coat papers.

10 Background Art

Ink jet recording is a method wherein an ink composition is ejected as a droplet through a fine nozzle to record letters or figures onto the surface of a recording medium. Ink jet recording systems which have been developed and put to practical use include: a method wherein an electric signal is converted to a mechanical signal using an electrostrictive element to intermittently eject an ink composition reservoir in a nozzle head section, thereby recording letters or symbols on the surface of a recording medium and a method wherein an ink composition, reservoir in a nozzle head section, in its portion very close to the ejection portion is rapidly heated to create a bubble and the ink composition is intermittently ejected by volume expansion created by the bubble to record letters or symbols on the surface of a recording medium.

20 Properties required of ink compositions used in the above ink jet recording are such that the drying property of the print is good, no feathering is created, good printing can be performed on various recording media, and, in the case of multi-color printing, color-to-color intermixing does not occur.

In particular, prevention of feathering is important for realizing a high-quality image. Paper is likely to create feathering because it comprises fibers that are different from each other or one another in ink penetration. In particular, this 25 tendency is significant for recycled paper because it comprises various fibers having different ink penetration. For this reason, in order to prevent the feathering, various proposals have been made on a reduction in penetration of the ink composition into recording media or an improvement in drying speed of the printed ink image.

30 For example, Japanese Patent Publication 2907/1990 proposes utilization of glycol ether as a wetting agent, Japanese Patent Publication 15542/1989 proposes utilization of a water-soluble organic solvent, and Japanese Patent Publication 3837/1990 proposes utilization of a glycol ether as a dye solubilizer.

Further, in order to improve the penetrability of an ink for ink jet recording, U.S. Patent No. 5,156,675 proposes addition of diethylene glycol monobutyl ether, U.S. Patent No. 5,183,502 proposes addition of Surfynol 465 (manufactured by Nissin Chemical Industry Co., Ltd.) as an acetylene glycol surfactant, and U.S. Patent No. 5,196,056 discloses addition of both diethylene glycol mono-n-butyl ether and Surfynol 465. Furthermore, U.S. Patent No. 2083372 studies 35 and teaches utilization of an ether of diethylene glycol as an ink composition. In this connection, diethylene glycol mono-n-butyl ether is known as butylcarbitol to those skilled in the art, and detailed description thereon is given, for example, in U.S. Patent No. 3,291,580.

40 For regulating the penetrability of the ink composition containing a pigment, for example, Japanese Patent Laid-Open No. 147861/1981 discloses utilization of a pigment and triethylene glycol monomethyl ether in combination. Japanese Patent Laid-Open No. 111165/1997 discloses utilization of a pigment and an ether of ethylene glycol, diethylene glycol, or triethylene glycol in combination.

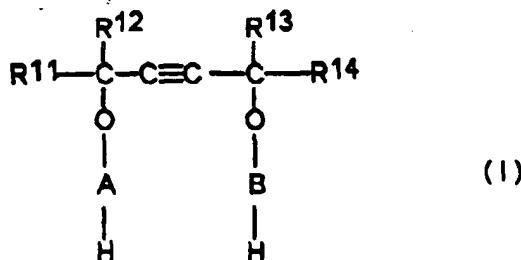
45 On the other hand, a method has been proposed wherein an ink composition is printed on a heated recording medium to rapidly evaporate the solvent component, thereby permitting the ink composition to be rapidly fixed onto the recording medium. Heating, however, is likely to have an adverse effect on recording media, particularly paper. Further, this method involves an additional disadvantage of increased power consumption by heating.

SUMMARY OF THE INVENTION

50 The present inventors have now found that an ink composition comprising a compound having a specific structure, when used in ink jet printing, can realize a good image having good drying speed and no significant feathering on various recording media, especially recycled papers.

Accordingly, an object of the present invention is to provide an ink composition that can realize a good image on various recording media, especially plain papers.

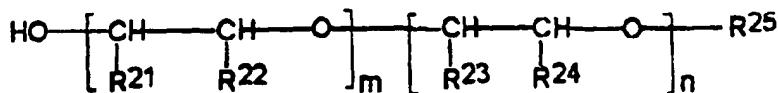
55 Thus, according to one aspect of the present invention, there is provided an ink for ink jet recording, comprising at least a water-soluble colorant, a water-soluble organic solvent, water, and a compound represented by the following formula (I), (II), or (III):



wherein

15 R^{11} , R^{12} , R^{13} , and R^{14} each independently represent a C_{1-6} alkyl group,
 A and B each independently represent a group consisting of an ethyleneoxy group and/or a propyleneoxy group,
 provided that any one of A and B contains at least one propyleneoxy group, and
 the total number of ethyleneoxy groups and propyleneoxy groups is 2 to 60;

20



(II)

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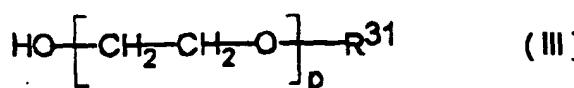
wherein

any one of R^{21} and R^{22} represents H with the other substituent representing CH_3 or H, and any one of R^{23} and R^{24} represents H with the other substituent representing CH_3 or H,
 35 when any one of R^{21} and R^{22} represents H, both R^{23} and R^{24} represent H, and
 when both R^{21} and R^{22} represent H, at least one of R^{23} and R^{24} represents CH_3 ,
 R^{25} represents a C_{4-10} alkyl group, and
 m and n each are a number satisfying $2 \leq m + n \leq 6$;
 provided that the compounds where R^{21} , R^{22} , R^{23} , and R^{24} all represent H are excluded,

40

and

45



50 wherein R^{31} represents a C_{4-10} alkyl group and p is an integer of 3 to 6.

DETAILED DESCRIPTION OF THE INVENTION

55

Ink for ink jet recording
 The term "ink for ink jet recording" used herein refers to a black ink in the case of monochrome printing, and, in the case of color printing, color inks, specifically a yellow ink, a magenta ink, and a cyan ink, and, in some cases, a black ink.

The ink for ink jet recording to be used in the present invention comprises at least a water-soluble colorant, a water-soluble organic solvent, water, and a compound represented by the formula (I), (II), or (III).

Compound represented by the formula (I), (II), or (III)

5 The ink composition comprising a compound represented by the formula (I), (II), or (III) according to the present invention can realize a good image, which has high drying speed and no significant feathering, on various recording media, especially on plain papers, particularly even on recycled papers. The compound represented by the formula (I), (II), or (III) appears to function as a surfactant in the ink composition. It is considered that the addition of these compounds permits the penetrability of the ink composition into the recording medium to be brought to a proper range for providing good drying speed and preventing the creation of feathering. Further, the addition of the above compounds can offer an additional advantage that ink jet recording can be stably carried out.

10 In the formula (I), R¹¹, R¹², R¹³, and R¹⁴ each independently represent a C₁₋₆ alkyl group, preferably a C₁₋₄ alkyl group. This alkyl group may be either a straight chain or a branched chain.

15 A and B each independently represent an ethyleneoxy group and/or a propyleneoxy group, provided that one of A and B contains at least one propyleneoxy group. The total number of ethyleneoxy groups and propyleneoxy groups is preferably 2 to 60, more preferably 4 to 10.

20 The number of carbon atoms of the alkyl group represented by R¹¹, R¹², R¹³, and R¹⁴, a combination of the alkyl group and the number of carbon atoms, the structure and a combination of A and B, and the total number of ethyleneoxy groups and propyleneoxy groups may be properly determined by taking into consideration the HLB value of the compound represented by the formula (I).

25 According to a preferred embodiment of the present invention, the HLB value of the compound represented by the formula (I) is preferably not less than 7. Compounds, represented by the formula (I), that can provide such HLB values include:

compounds wherein R¹¹ represents t-butyl, R¹² represents methyl, R¹³ represents t-butyl, R¹⁴ represents methyl, A represents -(CH₂-CH₂-O)-j-(CH₂-CH(CH₃)-O)-k-, B represents -(CH₂-CH₂-O)-j-(CH₂-CH(CH₃)-O)-k- where J=10 and k=2;

30 compounds wherein R¹¹ represents ethyl, R¹² represents methyl, R¹³ represents ethyl, R¹⁴ represents methyl, A represents -(CH₂-CH(CH₃)-O)-j-(CH₂-CH₂-O)-k-, B represents -(CH₂-CH(CH₃)-O)-j-(CH₂-CH₂-O)-k- where j = 1 and k = 10; and

35 compounds wherein R¹¹ represents isopropyl, R¹² represents ethyl, R¹³ represents isopropyl, R¹⁴ represents ethyl, A represents -(CH₂-CH₂-O)-j-(CH₂-CH(CH₃)-O)-k-(CH₂-CH₂-O)-l-, B represents -(CH₂-CH₂-O)-j-(CH₂-CH(CH₃)-O)-k-(CH₂-CH₂-O)-l- where j = 20, k = 1, and l = 4.

40 The use of a compound represented by the formula (I) has an advantage that foaming of the ink composition can be effectively prevented. The foaming of the ink composition leads to dropouts in ink jet recording, and hence should be preferably prevented. In particular, an ink composition containing an emulsion described below is often likely to foam. The addition of the compound represented by the formula (I) can effectively prevent foaming even in the ink composition containing an emulsion.

45 The amount of the compound represented by the formula (I) added in the ink for ink jet recording according to the present invention is preferably about 0.1 to 10% by weight.

The ink for ink jet recording according to the present invention is soluble in water. Therefore, preferably, the surfactant used is soluble in water and has a high HLB value. In particular, the HLB value of the compound represented by the formula (I) is preferably not less than 7, particularly preferably not less than 9. When the HLB value of the compound represented by the formula (I) is low, it is preferred to additionally use other surfactant(s) or a water-soluble organic solvent.

50 In the formula (II), any one of R²¹ and R²² represents H with the other substituent representing CH₃ or H, and any one of R²³ and R²⁴ represents H with the other substituent representing CH₃ or H, provided that R²¹, R²², R²³, and R²⁴ do not simultaneously represent H; when any one of R²¹ and R²² represents H, both R²³ and R²⁴ represent H; and when both R²¹ and R²² represent H, at least one of R²³ and R²⁴ represents CH₃, and R²⁵ represents a C₄₋₁₀ alkyl group that may be of a straight-chain type or a branched type with the branched type being preferred.

55 In order to lower the viscosity of the ink, it is desired for m + n to satisfy 2 ≤ m + n ≤ 6, preferably 2 ≤ m + n ≤ 3.

Preferred examples of compounds represented by the formula (II) include:

compounds wherein R²¹ represents hydrogen, R²² represents methyl, R²³ represents hydrogen, R²⁴ represents methyl, R²⁵ represents butyl, and m + n is 3;

compounds wherein R²¹ represents hydrogen, R²² represents methyl, R²³ represents methyl, R²⁴ represents

hydrogen, R²⁵ represents butyl, and m + n is 2; and compounds wherein R²¹ represents methyl, R²² represents hydrogen, R²³ represents methyl, R²⁴ represents hydrogen, R²⁵ represents butyl, and m + n is 6.

5 Use of the compound represented by the formula (II) can offer an advantage that the viscosity of the ink composition can be maintained at a low value. Maintaining the viscosity of the ink composition at a low value enables the amount of the colorant added to the ink composition to be increased. This can realize an image having a high print density.

In the ink for ink jet recording according to the present invention, the amount of the compound represented by the formula (II) is preferably in the range of 0.5 to 30% by weight.

10 In the formula (III), R³¹ represents a C₄₋₁₀ alkyl group. This alkyl group may be either a straight chain or a branched chain. According to a preferred embodiment of the present invention, use of a compound represented by the formula (III), wherein R³¹ represents an isobutyl or a t-butyl group, in the ink for ink jet recording is preferred.

15 As with the use of the compound represented by the formula (II), the use of the compound represented by the formula (III) enables the viscosity of the ink composition to be maintained at a low value, so that the amount of the colorant added can be increased.

The compound represented by the formula (III) often exhibits low water solubility. In this case, addition of a glycol ether, a nonionic surfactant, an amphoteric surfactant, or a mixture of two or more of them can improve the solubility of the compound represented by the formula (III) in the ink composition. In particular, addition of diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether is preferred.

20 In the ink for ink jet recording according to the present invention, the amount of the compound represented by the formula (III) added is preferably in the range of from 3 to 30% by weight.

Further, according to a preferred embodiment of the present invention, addition of a mixture of a plurality of compounds represented by the formula (III) to the ink composition is also preferred.

25 Water-soluble colorant

The water-soluble colorant contained in the ink according to the present invention may be either a dye or a pigment.

Dyes usable herein include various dyes commonly used in ink jet recording, such as direct dyes, acid dyes, food dyes, basic dyes, reactive dyes, disperse dyes, vat dyes, soluble vat dyes, and reactive disperse dyes.

30 Inorganic pigments or organic pigments may be used without any particular limitation. Inorganic pigments usable herein include, in addition to titanium oxide and iron oxide, carbon blacks produced by known processes, such as contact, furnace, and thermal processes. Examples of the organic pigments usable herein include azo pigments (including azo lake, insoluble azo pigment, condensed azo pigment, and chelate azo pigment), polycyclic pigments (for example, phthalocyanine, perylene, perinone, anthraquinone, quinacridone, dioxazine, thioindigo, isoindolinone, and quinophthalone pigments), dye chelates (for example, basic dye chelates and acid dye chelates), nitro pigments, nitroso pigments, and aniline black.

35 According to a preferred embodiment of the present invention, the pigment is dispersible and/or soluble in water without a dispersant. This pigment is one which has been surface treated so that at least one functional group, selected from carbonyl, carboxyl, hydroxyl, and sulfone groups, or a salt thereof is bonded to the surface of the pigment, thereby permitting the pigment to be dispersible and/or soluble in water without a dispersant. Specifically, this pigment can be prepared by grafting a functional group or a molecule containing a functional group onto the surface of carbon black by physical treatment, such as vacuum plasma, or chemical treatment. In the present invention, a single type or a plurality of types of functional groups may be grafted onto one carbon black particle.

40 The type of the functional group to be grafted and the degree of grafting may be suitably determined by taking the dispersion stability in the ink composition, the color density, the drying property at the front face of the ink jet head and the like into consideration.

45 In the present invention, when the pigment is stably present in water without any dispersant, this state is expressed as the state of "dispersion and/or dissolution." Not infrequently, it is difficult to distinguish the state of dissolution of a material from the state of dispersion of the material. In the present invention, any pigment can be used so far as the 50 pigment is stably present in water without any dispersant independently of whether the pigment is in a dispersion form or a solution form. In the present specification, a pigment, which can stably exist in water without any dispersant is often referred to as a "water-soluble pigment." The water-soluble pigment in this case, however, does not exclude a pigment which is in the state of dispersion in water.

55 According to a preferred embodiment of the present invention, the pigment is used as a pigment dispersion having an average particle diameter of 50 to 200 nm and a degree of dispersion of not more than 10.

The pigment, which is preferably used in the present invention, may be prepared, for example, by a method disclosed in Japanese Patent Laid-Open No. 3498/1996. Further, the above pigment may be a commercially available one, and preferred examples thereof include Microjet CW1 manufactured by Orient Chemical Industries, Ltd.

The amount of the pigment added to the ink composition is preferably 3 to 30% by weight, more preferably about 5 to 17% by weight.

Water-soluble organic solvent

5 Examples of the water-soluble organic solvent contained in the ink composition according to the present invention include: alkyl alcohols having 1 to 4 carbon atoms, such as ethanol, methanol, butanol, propanol, and isopropanol; glycol ethers, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxybutanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-iso-propyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-iso-propyl ether, dipropylene glycol mono-n-butyl ether, and dipropylene glycol mono-t-butyl ether; formamide; acetamide; dimethyl sulfoxide; sorbitan; acetin; diacetin; triacetin; and sulfolane.

10 The amount of the water-soluble organic solvent added to the ink composition is preferably 1 to 30% by weight, more preferably about 3 to 15% by weight.

Water and other ingredients

15 In the ink composition according to the present invention, water serves as a main solvent. Water may be pure water, such as ion-exchanged water, water purified by ultrafiltration or reverse osmosis, or distilled water or ultrapure water. Further, use of water, which has been sterilized by ultraviolet irradiation, by addition of hydrogen peroxide, or by other methods, is preferred because, when the ink is stored for a long period of time, such water can prevent the occurrence of mold and bacteria.

20 According to a preferred embodiment of the present invention, addition of a water-soluble glycol to the ink is preferred. Preferred water-soluble glycols usable herein include, for example, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polyethylene glycol having a molecular weight of not more than 2000, 1,3-propylene glycol, isopropylene glycol, isobutylene glycol, 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, mesoerythritol, and pentaerythritol. Water-soluble glycols function to prevent the ink from drying in the front face of nozzles.

25 The amount of the glycol added to the ink composition is preferably 1 to 30% by weight, more preferably about 3 to 15% by weight.

30 According to a preferred embodiment of the present invention, various saccharides may also be used in the ink. Preferred saccharides usable herein include monosaccharides and polysaccharides. More specific examples thereof include glucose, mannose, fructose, ribose, xylose, arabinose, lactose, galactose, aldonic acid, glucitose, maltose, cellobiose, sucrose, trehalose, maltotriose, alginic acid and salts thereof, cyclodextrins, and celluloses. The amount of the 35 saccharide added to the ink is preferably about 0.05 to 30% by weight.

35 The addition of the saccharide can prevent a clogging phenomenon where the ink dries at the front end of the head and consequently clogs the head. In this connection, the amount of conventional saccharides, i.e., monosaccharides and polysaccharides, added to the ink is preferably about 3 to 20%. On the other hand, the amount of alginic acid and salts thereof, cyclodextrins, and celluloses added to the ink is preferably such that the low viscosity of the ink can be 40 maintained permitting proper printing.

45 According to a preferred embodiment of the present invention, the ink composition may further comprise a surfactant. Preferred surfactants which may be added to the ink composition are those having good compatibility with other ingredients of the ink composition, and, among the surfactants, those having high penetrability and good stability are preferred. Preferred examples thereof include amphoteric surfactants and nonionic surfactants. Examples of amphoteric surfactants usable herein include lauryldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, coconut oil fatty acid amide propyldimethylaminoacetic acid betaine, polyoctylpolyaminoethylglycine, and imidazoline derivatives. Examples of nonionic surfactants usable herein include 50 ether surfactants, such as polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene dodecylphenyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene oleyl ether, polyoxyethylene lauryl ether, polyoxyethylene alkyl ether, and polyoxyalkylene alkyl ether, polyoxyethyleneoleic acid, ester surfactants, such as polyoxyethyleneoleic ester, polyoxyethylenedistearic ester, sorbitan laurate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate, polyoxyethylene monoleate, and polyoxyethylene stearate, and fluorosurfactants, such as fluoroalkyl 55 esters and salts of perfluoroalkylcarboxylic acids. It is also possible to use acetylene glycol surfactants, and examples

of acetylene glycol surfactants usable herein include Surfynol 465, TG, and 104 (manufactured by Air Products and Chemicals) and modification products thereof. Addition of the surfactant permits the penetrability of the ink composition to be further efficiently regulated. Further, this can offer an additional advantage that the water solubility of the compounds represented by the formulae (I), (II), and (III) can be improved.

5 The amount of the surfactant added to the ink composition is preferably 0.01 to 5% by weight, more preferably about 0.1 to 3% by weight.

According to a preferred embodiment of the present invention, when the water-soluble colorant is a pigment, the ink may further comprise an emulsion. Addition of the emulsion can improve the fixation and rubbing/scratch resistance of the resultant print. Preferably, the emulsion comprises a continuous phase of water and a dispersed phase of acrylic 10 resin, methacrylic resin, styrene resin, urethane resin, acrylamide resin, or epoxy resin or a mixture of these resins. Particularly preferred is an emulsion wherein the dispersed phase comprises a resin composed mainly of acrylic acid and/or methacrylic acid. The resin is not limited by polymerization methods and may be, for example, a block copolymer, a random copolymer or the like. Further, preferably, the emulsion used in the ink composition of the present invention has a film forming property and has a lowest possible film forming temperature of preferably room temperature or 15 below, more preferably 0 to 20°C.

According to a preferred embodiment of the present invention, the resin component of the emulsion is a resin particle having a core/shell structure comprising a core surrounded by a shell. For example, the resin particle may be constructed so that a resin component capable of improving the drying to the touch and the fixation of the ink is incorporated into the core and a resin component, which permits resin particles to stably exist in the ink composition, is 20 incorporated into the shell. According to a preferred embodiment of the present invention, the shell comprises a resin having either a crosslinked structure or a structure with the number of benzene nuclei being larger than that in the structure of the core.

Materials for the shell usable herein include styrene, tetrahydrofurfuryl acrylate and butyl methacrylate, (α, 2, 3, or 4)-alkylstyrene, (α, 2, 3, or 4)-alkoxystyrene, 3,4-dimethylstyrene, α-phenylstyrene, divinylbenzene, vinylnaphthalene, 25 dimethylamino (meth)acrylate, dimethylaminoethyl (meth)acrylate, dimethylaminopropylacrylamide, N,N-dimethylaminoethyl acrylate, acryloylmorpholine, N,N-dimethylacrylamide, N-isopropylacrylamide, N,N-diethylacrylamide, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, ethylhexyl (meth)acrylate, and other alkyl (meth)acrylates, methoxydiethylene glycol (meth)acrylate, (meth)acrylate of an ethyl, propyl, or butyl ester of diethylene glycol or polyethylene glycol, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, isobornyl (meth)acrylate, 30 hydroxylalkyl (meth)acrylate, fluorine-, chlorine-, or silicon-containing (meth)acrylate, (meth)acrylamide, and maleic amide.

When a crosslinked structure is introduced in addition to the above (meth)acrylic acid, it is possible to use (mono, di, tri, tetra, or poly)ethylene glycol di(meth)acrylate, (meth)acrylates of 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol, trimethylolpropane tri(meth)acrylate, glycerin (di or tri)(meth)acrylate, 35 di(meth)acrylate of ethylene oxide adduct of bisphenol A or F, neopentyl glycol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, and dipentaerythritol hexa(meth)acrylate.

For the formation of the core, the same material as used in the formation of the shell may be used.

Emulsifiers usable for the formation of the above polymeric fine particles include sodium laurylsulfate, potassium laurylsulfate, anionic surfactants, nonionic surfactants, and amphoteric surfactants, which are commonly used in the 40 art.

Polymerization initiators usable herein include potassium persulfate, ammonium persulfate, hydrogen persulfate, azobisisobutyronitrile, benzoyl peroxide, dibutyl peroxide, peracetic acid, cumene hydroperoxide, t-butyl hydroperoxide, and p-menthane hydroperoxide.

Chain transfer agents usable for the polymerization include t-dodecylmercaptan, n-dodecylmercaptan, n-octylmercaptan, xanthogen compound, such as dimethylxanthogendisulfide or diisobutylxanthogendisulfide, dipentene, indene, 45 1,4-cyclohexadiene, dihydrofuran, and xanthen.

According to a preferred embodiment of the present invention, the molecular weight of the emulsion is preferably not less than 1000, more preferably about 10,000 to 100,000.

The emulsion used in the present invention may be a commercially available one, and examples thereof include 50 Z116 manufactured by Mitsui Toatsu Chemicals, Inc.

The amount of the water-soluble emulsion added may be properly determined. For example, it is preferably about 0.5 to 10% by weight, more preferably about 3 to 5% by weight.

The ink composition of the present invention may contain, in addition to the above ingredients, other ingredients. Examples of other ingredients usable herein include preservatives, antioxidants, electric conductivity adjustors, pH 55 adjustors, viscosity modifiers, surface tension modifiers, oxygen absorbers, and nozzle clogging preventives.

Preservatives and fungicides usable herein include, for example, sodium benzoate, pentachlorophenol sodium, 2-pyridinethiol-1-oxide sodium, sodium sorbate, sodium dehydroacetate, 1,2-dibenzothiazoline-3-one (Proxel CRL, Proxel BDN, Proxel GXL, Proxel XL-2, and Proxel TN, manufactured by ICI).

pH adjustors, solubilizers, and antioxidants usable herein include: amines, such as diethanolamine, triethanolamine, propanolamine, and morpholine, and modification products thereof; inorganic salts, such as potassium hydroxide, sodium hydroxide, and lithium hydroxide; ammonium hydroxide; quaternary ammonium hydroxide, such as tetramethylammonium; salts of carbonic acid, such as potassium carbonate, sodium carbonate, and lithium carbonate; salts of phosphoric acid, such as potassium phosphate, sodium phosphate, and lithium phosphate; N-methyl-2-pyrrolidone; urea compounds, such as urea, thiourea, and tetramethylurea; allophanate compounds, such as allophanate and methyl allophanate; biuret compounds, such as biuret, dimethylbiuret, and tetramethylbiuret; and L-ascorbic acid and salts thereof.

5 Antioxidants and ultraviolet absorbers, which may be added to the ink, include Tinuvin 328, 900, 1130, 384, 292, 10 123, 144, 622, 770, and 292, Irgacor 252 and 153, and Irganox 1010, 1076, 1035, and MD1024, manufactured by Ciba-Geigy, and lanthanide oxides.

10 Viscosity modifiers usable herein include rosin compounds, alginic acid compounds, polyvinyl alcohol, hydroxypropyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, salts of polyacrylic acid, polyvinyl pyrrolidone, gum arabic, and starch.

15 Ink jet recording method and apparatus

The ink jet recording method used in the ink composition according to the present invention refers to a recording method wherein a droplet of an ink composition is ejected and deposited onto a recording medium to perform printing.

20 Examples of such ink jet recording methods include, for example, a method wherein an electric signal is converted to a mechanical signal using an electrostrictive element to intermittently eject an ink reservoird in a nozzle head section, thereby recording letters or symbols on the surface of a recording medium, and a method wherein an ink, reservoird in a nozzle head section, in its portion very close to the ejection portion is rapidly heated to create a bubble and the ink is intermittently ejected by volume expansion created by the bubble to record letters or symbols on the surface of a recording medium. According to a preferred embodiment of the present invention, the ink of the present invention is used in ink jet recording using an electrostrictive element. This is because methods involving heating of the head section cause the colorant and other ingredients contained in the ink to be decomposed, clogging the head.

25 An ink, comprising a pigment as the colorant, having a relatively high content of a solid, like the ink of the present invention, when placed in a nozzle without ejection for a long period of time, is likely to dry at the front face of the nozzle to cause thickening, leading to an ink droplet trajectory directionality problem. In this case, slightly moving the ink with care not to cause the ink to be delivered from the front face of the nozzle can stir the ink, permitting the ink to be stably ejected. This can be achieved by pressurizing the ink, by means of pressurizing means for ejecting the ink, with care not to cause the ink to be ejected. In the above regulation, use of an electrostrictive element as the pressurizing means is preferred from the viewpoint of easy regulation. Utilization of this mechanism can increase the content of the pigment 30 in the ink, permitting a high color density to be provided using a pigment-based ink and, in addition, the ink to be stably ejected.

35 When the above slight moving of the ink is carried out in the nozzle face of an ink jet recording apparatus, this operation is effective for an ink composition having a pigment content of about 5 to 15% by weight, more preferably about 7 to 10% by weight.

40 In use, the ink composition of the present invention may be filled into an ink tank constructed so that a polyurethane foam is provided therein and the ink comes into contact with the polyurethane foam. In this case, the glycol ether compound, which is preferably used in the present invention, and the acetylene glycol surfactant used in the present invention are adsorbed onto the polyurethane foam. Therefore, preferably, they are added in an excessive amount in consideration of the adsorption. Further, the polyurethane foam can ensure a negative pressure by using the ink composition of the present invention and is less likely to be decomposed by ingredients of the ink used in the present invention, or to create a deposit causative of clogging of the nozzle. A polyurethane foam not using a curing catalyst containing a metal salt or a cationic material is preferred. Specifically, use of a polyurethane foam comprising a poly-functional isocyanate, such as tolylene diisocyanate or m-xylene diisocyanate, and a material having a plurality of hydroxyl groups, such as a glycol compound having an average molecular weight of about 300 to 3000, such as polypropylene glycol or polyethylene glycol, glycerin, pentaerythritol, dipentaerythritol, neopentyl glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, or 1,5-pentanediol, is preferred from the viewpoint of ensuring negative pressure, by virtue of the stability of foam shape, and chemical stability.

45 When the acetylene glycol surfactant is utilized, a part of the acetylene glycol surfactant is adsorbed onto the polyurethane foam. Therefore, when the acetylene glycol surfactant is added to the ink composition, the composition of the ink should be determined by taking into consideration the amount of the acetylene glycol surfactant adsorbed onto the urethane foam.

50 According to a preferred embodiment of the present invention, the ink composition of the present invention is printed by ejecting a droplet of the ink composition through a nozzle the front end (head) of which has a water-repellent

surface. More specifically, the front end of the nozzle preferably has a structure produced by providing a stainless steel material as a base material, applying an eutectoid plating of tetrafluoroethylene and nickel on the base, and heat-treating the plating to form a water-repellent layer. In addition, utilization of an eutectoid plating of tetrafluoroethylene and a highly non-oxidizable metal, such as chromium, titanium, gold, platinum, silver, or iridium, instead of nickel is also preferred. A combination of the ink composition according to the present invention with the above nozzle enables continuous printing to be stably performed for a long period of time.

According to a more preferred embodiment of the present invention, the contact angle of the ink composition on the water-repellent surface at the front end of the nozzle is 50°C or above at a general operation temperature of the printer (for example, 15 to 60°C). According to this embodiment, improved print quality and continuous printing can be realized.

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EXAMPLES

The present invention will be described in more detail with reference to the following examples though it is not limited to these examples only.

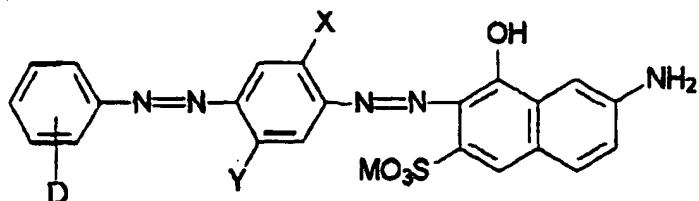
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Preparation of ink compositions

Water-soluble pigments 1 to 4 used in the following examples are water-soluble pigments each having on its surface a group terminated with a carbonyl, carboxyl, hydroxyl, sulfone or other group. These pigments were prepared by 20 applying a method described in Japanese Patent Laid-Open No. 34981/1996 to a carbon black having a particle diameter of 10 to 300 nm and a degree of dispersion of not more than 10. The water-soluble pigments had an average particle diameter as indicated in parentheses (unit: nm).

Further, water-soluble dyes used in the following examples are represented by the following general formula (IV) and (V):

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(IV)

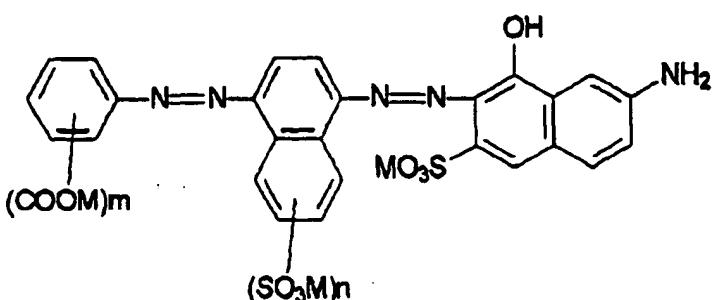
35

wherein

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D represents $\text{PO}(\text{OM})_2$ or COOM ,
 X and Y each independently represents an alkoxy or alkyl group, and
 M represents an alkali metal, H, NH_4 , or an organic amine; and

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(V)

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wherein

M represents an alkali metal, H, NH₄, or an organic amine,

m is an integer of 1 or 2, and

n is an integer of 0 or 1.

5 Abbreviations used in the following description are as follows.

DEGmBE: diethylene glycol mono-n-butyl ether

DMI: 1,3-dimethyl-2-imidazolidinone

PGmBE: propylene glycol mono-n-butyl ether

10 MPD: 2-methyl-2,4-pentanediol

DPGmBE: dipropylene glycol mono-n-butyl ether

TEGmBE: triethylene glycol mono-n-butyl ether

Further, in the following description, the term "emulsion" refers to a resin emulsion comprising fine particles of a 15 polymer dispersed in water, and the emulsion was prepared as follows.

Ion-exchanged water (100 parts) was placed in a reactor equipped with a dropping device, a thermometer, a water cooling type reflux condenser, and an agitator. Potassium persulfate (0.2 part) as a polymerization initiator was added thereto at 70°C in a nitrogen atmosphere while stirring. Thereafter, a monomer solution prepared by dissolving 0.05 part of sodium laurylsulfate, 10 parts of styrene, 2 parts of tetrahydrofurfuryl acrylate, 5 parts of butyl methacrylate, and 0.02 20 part of t-dodecylmercaptan in 7 parts of ion-exchanged water was added dropwise thereto at 70°C to conduct a reaction, thereby preparing a primary compound. A 10% solution of ammonium persulfate (2 parts) was added to the primary compound with stirring. Further, a reaction solution composed of 30 parts of ion-exchanged water, 10 parts of diethylene glycol monobutyl ether, 0.2 part of potassium laurylsulfate, 30 parts of styrene, 15 parts of butyl methacrylate, 16 parts of butyl acrylate, 3 parts of acrylic acid, 1 part of 1,6-hexanediol dimethacrylate, and 0.5 part of t-dodecylmercaptan was added to the mixture at 70°C with stirring to conduct polymerization. The reaction mixture was 25 then neutralized and adjusted to pH 8-8.5 by addition of ammonia and filtered through a 0.3 µm filter, thereby preparing a dispersion of fine particles of a polymer in water as an emulsion.

Into all the following ink compositions were added 0.1 to 1% by weight of Proxel XL-2 as a corrosion preventive for inks and 0.001 to 0.05% by weight of benzotriazole as a corrosion preventive for an ink jet head member.

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Example A

35	Example A1	Amount (wt%)
	Water-soluble pigment 1 (105)	5.0
	Compound 1 of the formula (I)	1.0
40	Emulsion	3.0
	DEGmBE	7.0
	Glycerin	6.0
	1,5-Pentanediol	5.0
45	Triethanolamine	0.8
	Ion-exchanged water	Balance

50 Compound 1 of the formula (I) is a compound wherein R¹¹ and R¹² represent a methyl group, R¹³ and R¹⁴ represent an isobutyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 4, the average number of units of the ethylene oxide group is 6, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 10.

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Example A2	Amount (wt%)
Water-soluble pigment 2 (85)	3.0
Compound 2 of the formula (I)	1.2
Emulsion	1.0
DEGmBE	10.0
Dipropylene glycol	5.0
Triethanolamine	1.0
Potassium hydroxide	0.1
Ion-exchanged water	Balance

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Example A3	Amount (wt%)
Water-soluble pigment 3 (90)	5.5
Compound 3 of the formula (I)	1.4
Emulsion	10.0
Propylene glycol	7.0
Triethylene glycol	3.0
Ion-exchanged water	Balance

Compound 2 of the formula (I) is a compound wherein R¹¹ and R¹² represent an ethyl group, R¹³ and R¹⁴ represent a methyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 2, the average number of units of the ethylene oxide group is 6, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 10.

Compound 3 of the formula (I) is a compound wherein R¹¹, R¹², R¹³, and R¹⁴ represent a methyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 4, the average number of units of the ethylene oxide group is 10, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 14.

Example A4	Amount (wt%)
Water-soluble pigment 4 (80)	5.0
Compound 4 of the formula (I)	0.8
Emulsion	3.0
1,6-Hexanediol	5.0
Tripropylene glycol	2.0
DMI	2.0
Sodium benzoate	0.1
Ion-exchanged water	Balance

Compound 4 of the formula (I) is a compound wherein R¹¹ and R¹² represent a methyl group, R¹³ and R¹⁴ repre-

sent an isopropyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 3, the average number of units of the ethylene oxide group is 9, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 12.

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	Example A5	Amount (wt%)
10	Water-soluble pigment 1	3.0
	Water-soluble dye A1	1.0
	Compound 5 of the formula (I)	1.2
	Emulsion	3.5
15	PGmBE	2.0
	MPD	3.0
	1,5-Pentanediol	3.0
	Triethanolamine	0.9
20	Ion-exchanged water	Balance

Compound 5 of the formula (I) is a compound wherein R¹¹ and R¹² represent a methyl group, R¹³ and R¹⁴ represent an isobutyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 4, the average number of units of the ethylene oxide group is 12, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 16. The water-soluble dye A1 is a compound represented by the formula (IV), wherein A represents COOK, X and Y represent a methyl group, and M represents potassium.

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	Example A6	Amount (wt%)
35	Water-soluble dye A2	5.0
	Compound 6 of the formula (I)	0.5
	Emulsion	4.0
	DPGmBE	2.0
40	DEGmBE	10.0
	Neopentyl glycol	5.0
	Ion-exchanged water	Balance

Compound 6 of the formula (I) is a compound wherein R¹¹ and R¹² represent a methyl group, R¹³ and R¹⁴ represent an n-propyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 2, the average number of units of the ethylene oxide group is 4, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 6. The water-soluble dye A2 is a compound represented by the formula (V), wherein m is 1, n is 1, and M represents potassium.

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	Example A7	Amount (wt%)
	Direct Blue 86	5.0
	Compound 7 of the formula (I)	1.6

(continued)

Example A7	Amount (wt%)
Emulsion	5.0
TEGmBE	10.0
Glycerin	5.0
Trimethylolpropane	5.0
Triethanolamine	0.1
Ion-exchanged water	Balance

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Example A8	Amount (wt%)
Acid Red 52	5.5
Compound 8 of the formula (I)	1.0
Emulsion	5.0
DPGmBE	5.0
DEGmBE	5.0
Diethylene glycol	5.0
Sodium dodecylbenzenesulfonate	0.2
Ion-exchanged water	Balance

Compound 7 of the formula (I) is a compound wherein R¹¹ and R¹² represent a methyl group, R¹³ and R¹⁴ represent an isobutyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 10, the average number of units of the ethylene oxide group is 40, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 50.

Compound 8 of the formula (I) is a compound wherein R¹¹ and R¹² represent a methyl group, R¹³ and R¹⁴ represent an isobutyl group, and A and B each represent a group consisting of propylene oxide and ethylene oxide wherein the average number of units of the propylene oxide group is 1, the average number of units of the ethylene oxide group is 1, and the average total number of units of the ethylene oxide group and units of the propylene oxide group is 2.

Comparative Example A

In the following comparative examples, the term "pigment dispersion" refers to a carbon black which has been dispersed with the aid of a styrene/acrylic acid random copolymer as a dispersant, and the average particle diameter thereof was as indicated in parentheses (unit: nm).

Comparative Example A1	Amount (wt%)
Pigment dispersion (90)	5.0
Dispersant	3.0
Nonionic surfactant	0.8
2-Pyrrolidone	3.0
Polyethylene glycol 1000	4.0
Ion-exchanged water	Balance

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5	Comparative Example A2	Amount (wt%)
10	Food Black 2	5.5
	Glycerin	10.0
	Ethyl carbitol	10.0
	2-Pyrrolidone	5.0
	Ion-exchanged water	Balance

15	Comparative Example A3	Amount (wt%)
20	Pigment dispersion (110)	5.5
	Water-soluble dye (Food Black 2)	2.5
	Diethylene glycol	10.0
	Nonionic surfactant	1.0
	Ion-exchanged water	Balance

25 Print quality test

Characters were printed using the ink compositions prepared in the examples and the comparative examples by means of an ink jet printer MJ-930C (manufactured by Seiko Epson Corp.). Papers used for the evaluation were Conqueror, Favorit, Modo Copy, Rapid Copy, EPSON EPP, Xerox 4024, Xerox 10, Neenah Bond, Ricopy 6200, Yamayuri, and Xerox R papers that are plain papers commercially available in Europe, America, and Japan.

30 The prints were evaluated as follows. Assuming that 10 to 50 mg of a spherical ink droplet was spread in a circular form on the surface of paper, the radius of an circumscribed circle, r_2 , to the radius of an inscribed circle, r_1 , that is, r_2/r_1 , in the formed ink dot was determined. The results were evaluated according to the following criteria.

35 A: $r_2/r_1 \leq 2.0$
 B: $2.0 < r_2/r_1 \leq 4.0$
 C: $4.0 < r_2/r_1 \leq 6.0$
 D: $6.0 < r_2/r_1$

40 The results of evaluation were as summarized in the following table.

Table 1

45		Results of evaluation on print quality								Comparative Example		
		1	2	3	4	5	6	7	8	1	2	3
50	Conqueror	A	A	A	A	A	A	A	A	C	C	C
	Favorit	A	A	A	A	A	A	A	A	D	D	D
	Modo Copy	A	A	A	A	A	A	A	A	C	D	D
	Rapid Copy	A	A	A	A	A	A	A	A	C	D	D
	EPSON EPP	A	A	A	A	A	A	A	A	C	C	D
55	Xerox P	A	A	A	A	A	A	A	A	C	D	D

Table 1 (continued)

Results of evaluation on print quality											
	Example								Comparative Example		
	1	2	3	4	5	6	7	8	1	2	3
5	Xerox 4024	A	A	A	A	A	A	A	C	D	D
10	Xerox 10	A	A	A	A	A	A	A	B	D	D
15	Neenha Bond	A	A	A	A	A	A	A	D	D	D
20	Ricopy 6200	A	A	A	A	A	A	A	B	C	D
25	Yamayuri	A	A	A	A	A	A	A	D	D	D
30	Xerox R	A	A	A	A	A	A	A	C	D	D

Example B

Example B1	Amount (wt%)
Water-soluble pigment 1 (105)	5.0
Compound 1 of the formula (II)	8.0
Emulsion	3.0
Glycerin	6.0
1,5-Pentanediol	5.0
Triethanolamine	0.8
Ion-exchanged water	Balance

Compound 1 of the formula (II) is a compound wherein both R²¹ and R²² represent H, one of R²³ and R²⁴ represents a methyl group with the other substituent representing H, R²⁵ represents butyl, and m + n is 2.

Example B2	Amount (wt%)
Water-soluble pigment 2 (85)	4.5
Compound 2 of the formula (II)	10.0
Emulsion	3.0
Dipropylene glycol	5.0
Surfynol 465	1.2
Triethanolamine	0.1
Ion-exchanged water	Balance

Compound 2 of the formula (II) is a compound wherein one of R²¹ and R²² represents a methyl group with the other substituent representing H, both R²³ and R²⁴ represent H, R²⁵ represents butyl, and m + n is 2.

Example B3	Amount (wt%)
Water-soluble pigment 3 (90)	5.5
Compound 3 of the formula (II)	10.0
Emulsion	10.0
Propylene glycol	7.0
Triethylene glycol	3.0
1,6-Hexanediol	5.0
Potassium hydroxide	0.1
Ion-exchanged water	Balance

Compound 3 of the formula (II) is a mixture of a compound wherein both R²¹ and R²² represent H, and one of R²³ and R²⁴ represents a methyl group with the other substituent representing H, R²⁵ represents butyl, with a compound wherein one of R²¹ and R²² represents a methyl group with the other substituent representing H, and R²³ and R²⁴ represent H, R²⁵ represents butyl, provided that the average of m + n is 2.

Example B4	Amount (wt%)
Water-soluble pigment 4 (80)	5.0
Water-soluble dye B1	1.0
Compound 4 of the formula (II)	8.0
Emulsion	1.0
Tripropylene glycol	2.0
Dimethyl-2-imidazolidinone	2.0
Sodium benzoate	0.1
Ion-exchanged water	Balance

Compound 4 of the formula (II) is a mixture of a compound wherein both R²¹ and R²² represent H, one of R²³ and R²⁴ represents a methyl group with the other substituent representing H, R²⁵ represents butyl, with a compound wherein one of R²¹ and R²² represents a methyl group with the other substituent representing H and both R²³ and R²⁴ represent H, R²⁵ represents butyl, provided that the average of m + n is 3. The water-soluble dye B1 is a compound represented by the formula (IV), wherein A represents COOK, X and Y represent a methyl group, and M represents potassium.

Example B5	Amount (wt%)
Water-soluble pigment 1 (105)	3.0
Water-soluble dye B2	1.0
Compound 5 of the formula (II)	7.0
Emulsion	1.0
Triethanolamine	0.9
Ion-exchanged water	Balance

Compound 5 of the formula (II) is a mixture of a compound wherein both R²¹ and R²² represent H, one of R²³ and R²⁴ represents a methyl group with the other substituent representing H, R²⁵ represents butyl, with a compound wherein one of R²¹ and R²² represents a methyl group with the other substituent representing H and both R²³ and R²⁴ represent H, R²⁵ represents butyl, provided that the average of m + n is 4. The water-soluble dye B2 is a compound represented by the formula (IV), wherein A represents COONa, X and Y represent a methyl group, and M represents sodium.

10	Example B6	Amount (wt%)
15	Water-soluble dye 2	5.0
	Compound 6 of the formula (II)	6.0
	Glycerin	15.0
	Triethanolamine	0.9
	Ion-exchanged water	Balance

Compound 6 of the formula (II) is a mixture of a compound wherein both R²¹ and R²² represent H, one of R²³ and R²⁴ represents a methyl group with the other substituent representing H, R²⁵ represents butyl, with a compound wherein one of R²¹ and R²² represents a methyl group with the other substituent representing H and both R²³ and R²⁴ represent H, R²⁵ represents butyl, provided that the average m + n is 2.5. The water-soluble dye 2 is a compound represented by the formula (V), wherein m is 1, n is 1, and M represents potassium.

25	Example B7	Amount (wt%)
30	Direct Blue 86	5.0
	Compound 7 of the formula (II)	10.0
	Glycerin	5.0
35	Trimethylolpropane	5.0
	Trimethylethane	5.0
	Surfynol 465	1.0
	Triethanolamine	0.1
40	Ion-exchanged water	Balance

Compound 7 of the formula (II) is a mixture of a compound wherein both R²¹ and R²² represent H, and one of R²³ and R²⁴ represents a methyl group with the other substituent representing H, R²⁵ represents butyl, with a compound wherein one of R²¹ and R²² represents a methyl group with the other substituent representing H, and both R²³ and R²⁴ represent H, R²⁵ represents butyl, provided that the average of m + n is 6.

50	Example B8	Amount (wt%)
55	Acid Red 52	5.5
	Compound 8 of the formula (II)	6.0
	Diethylene glycol	5.0
	Tetrapropylene glycol	5.0
	Ion-exchanged water	Balance

Compound 8 of the formula (II) is a compound wherein both R²¹ and R²² represent H, one of R²³ and R²⁴ represents a methyl group with the other substituent representing H, R²⁵ represents butyl, and m + n is 3.

Comparative Example B

5 In the following comparative examples, the term "pigment dispersion" refers to a carbon black which has been dispersed with the aid of a styrene/acrylic acid random copolymer as a dispersant, and the average particle diameter thereof was as indicated in parentheses (unit: nm).

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Comparative Example B1	Amount (wt%)
Pigment dispersion (90)	5.0
Glycerin	10.0
Dispersant	3.0
Nonionic surfactant	1.0
Ion-exchanged water	Balance

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Comparative Example B2	Amount (wt%)
Food Black 2	5.5
DEGmME	7.0
Diethylene glycol	10.0
2-Pyrrolidone	5.0
Ion-exchanged water	Balance

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Comparative Example B3	Amount (wt%)
Water-soluble pigment 11 (110)	5.5
Food Black 2	2.5
Diethylene glycol	10.0
Nonionic surfactant	1.0
Ion-exchanged water	Balance

Print quality test

50 For the ink compositions prepared in Examples B1 to B8 and Comparative Examples B1 to B3, prints were prepared and evaluated for feathering in the same manner as described above in connection with the ink composition prepared in Examples A1 to A8 and Comparative Examples A1 to A3. The results were as summarized in the following table.

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Table 2

Results of evaluation on print quality											
	Example								Comparative Example		
	1	2	3	4	5	6	7	8	1	2	3
5	Conqueror	A	A	A	A	A	A	A	C	C	C
10	Favorit	A	A	A	A	A	A	A	D	D	D
15	Modo Copy	A	A	A	A	A	A	A	C	D	D
20	Rapid Copy	A	A	A	A	A	A	A	C	D	D
25	EPSON EPP	A	A	A	A	A	A	A	C	C	D
30	Xerox P	A	A	A	A	A	A	A	C	D	D
35	Xerox 4024	A	A	A	A	A	A	A	C	D	D
40	Xerox 10	A	A	A	A	A	A	A	B	D	D
45	Neenha Bond	A	A	A	A	A	A	A	C	D	D
50	Ricopy 6200	A	A	A	A	A	A	A	B	C	D
55	Yamayuri	A	A	A	A	A	A	A	D	D	D
60	Xerox R	A	A	A	A	A	A	A	C	D	D

Example C

Example C1	Amount (wt%)
Water-soluble pigment 1 (105)	5.0
Compound 1 of the formula (III)	8.0
DEGmBE	2.0
Emulsion	3.0
Glycerin	6.0
1,5-Pentanediol	5.0
Triethanolamine	0.8
Ion-exchanged water	Balance

45 Compound 1 of the formula (III) is a compound wherein R³¹ represents a neopentyl group and p is 3.

Example C2	Amount (wt%)
Water-soluble pigment 2 (85)	4.5
Compound 2 of the formula (III)	10.0
Emulsion	3.0
Dipropylene glycol	5.0
Surfynol 465	1.2
Triethanolamine	0.9

(continued)

Example C2	Amount (wt%)
Ion-exchanged water	Balance

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Compound 2 of the formula (III) is a compound wherein R³¹ represents a t-butyl group and p is 3.

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Example C3	Amount (wt%)
Water-soluble pigment 3 (90)	5.5
Compound 3 of the formula (III)	10.0
Emulsion	10.0
Diethylene glycol	7.0
Thiodiglycol	3.5
1,6-Hexanediol	5.0
Triethanolamine	1.0
Potassium hydroxide	0.1
Ion-exchanged water	Balance

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Compound 3 of the formula (III) is a compound wherein R³¹ represents an n-hexyl group and p is 3.

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Example C4	Amount (wt%)
Water-soluble pigment 4 (80)	5.0
Water-soluble dye C1	1.0
Compound 4 of the formula (III)	8.0
TEGmBE	3.0
Emulsion	1.0
Diethylene glycol	3.0
1,5-Pentanediol	2.0
Dimethyl-2-imidazolidinone	2.0
Sodium benzoate	0.1
Triethanolamine	0.7
Ion-exchanged water	Balance

Compound 4 of the formula (III) is a compound wherein R³¹ represents an isobutyl group and p is 3. The water-soluble dye C1 is a compound of the formula (IV) wherein A represents COOK, X and Y represent a methyl group, and M represents potassium.

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Example C5	Amount (wt%)
Water-soluble pigment 1 (105)	3.0

(continued)

Example C5	Amount (wt%)
Water-soluble dye C2	1.0
Compound 5 of the formula (III)	7.0
DEGmBE	2.0
Emulsion	1.0
Glycerin	14.0
Triethanolamine	0.9
Ion-exchanged water	Balance

15 Compound 5 of the formula (III) is a mixture of 50% of a compound wherein R³¹ represents an n-hexyl group and p is 3, with 50% of a compound wherein R³¹ represents an n-pentyl group and p is 3. The water-soluble dye C2 is a compound represented by the formula (IV), wherein A represents COONa, X and Y represent a methyl group, and M represents sodium.

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Example C6	Amount (wt%)
Water-soluble dye 2	5.0
Compound 6 of the formula (III)	6.0
TEGmBE	4.0
Glycerin	15.0
Thiodiglycol	2.0
1,5-Pentanediol	1.0
Triethanolamine	0.9
Ion-exchanged water	Balance

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Compound 6 of the formula (III) is a compound wherein R³¹ represents a 1,1-dimethylbutyl group and p is 3. The water-soluble dye 2 is a compound represented by the formula (V), wherein m is 1, n is 1, and M represents potassium.

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Example C7	Amount (wt%)
Direct Yellow 132	5.0
Compound 7 of the formula (III)	10.0
DEGmBE	3.0
Glycerin	5.0
Trimethylolpropane	5.0
Trimethylolethane	5.0
Surfynol 465	1.0
Triethanolamine	0.5
KOH	0.05
Ion-exchanged water	Balance

Compound 4 of the formula (III) is a mixture of 50% of a compound wherein R³¹ represents a 1,3-dimethylbutyl

group and p is 3, with 50% of a compound wherein R³¹ represents a 1,2-dimethylbutyl group and p is 3.

5	Example C8	Amount (wt%)
10	Acid Blue 9	5.5
	Compound 8 of the formula (III)	6.0
	Glycerin	5.0
	Diethylene glycol	5.0
	Tetrapropylene glycol	5.0
15	Triethanolamine	0.9
	KOH	0.1
	Ion-exchanged water	Balance

Compound 8 of the formula (III) is a mixture of 50% of a compound wherein R³¹ represents a neopentyl group and p is 3, with 30% of a compound wherein R³¹ represents an n-pentyl group and p is 3 and 20% of a compound wherein R³¹ represents an isopentyl group and p is 3.

Comparative Example C

25 In the following comparative examples, the term "pigment dispersion" refers to a carbon black which has been dispersed with the aid of a styrene/acrylic acid random copolymer as a dispersant, and the average particle diameter thereof was as indicated in parentheses (unit: nm).

30	Comparative Example C1	Amount (wt%)
35	Water-soluble pigment 9 (90)	5.0
	Glycerin	10.0
	Dispersant	3.0
	Nonionic surfactant	1.0
40	Ion-exchanged water	Balance

45	Comparative Example C2	Amount (wt%)
50	Food Black 2	5.5
	DEGmME	7.0
	Diethylene glycol	10.0
	2-Pyrrolidone	5.0
55	Ion-exchanged water	Balance

5	Comparative Example C3	Amount (wt%)
10	Water-soluble pigment 11 (110)	5.5
	Food Black 2	2.5
	Diethylene glycol	10.0
	Nonionic surfactant	1.0
	Ion-exchanged water	Balance

Print quality test

15 For the ink compositions prepared in Examples C1 to C8 and Comparative Examples C1 to C3, prints were prepared and evaluated for feathering in the same manner as described above in connection with the ink composition prepared in Examples A1 to A8 and Comparative Examples A1 to A3. The results were as summarized in the following table.

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Table 3

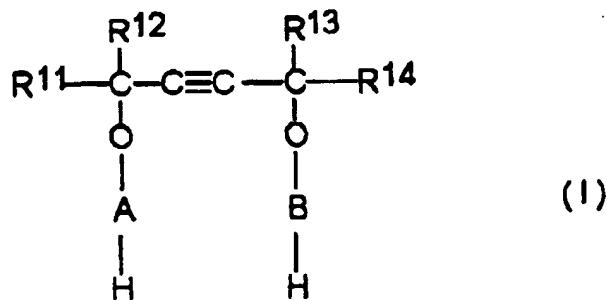
25		Results of evaluation on print quality								Comparative Example		
		1	2	3	4	5	6	7	8	1	2	3
30	Conqueror	A	A	A	A	A	A	A	A	C	C	C
	Favorit	A	A	A	A	A	A	A	A	D	D	D
	Modo Copy	A	A	A	A	A	A	A	A	C	D	D
	Rapid Copy	A	A	A	A	A	A	A	A	C	D	D
	EPSON EPP	A	A	A	A	A	A	A	A	C	C	D
	Xerox P	A	A	A	A	A	A	A	A	C	D	D
	Xerox 4024	A	A	A	A	A	A	A	A	C	D	D
	Xerox 10	A	A	A	A	A	A	A	A	B	D	D
	Neenha Bond	A	A	A	A	A	A	A	A	C	D	D
	Ricopy 6200	A	A	A	A	A	A	A	A	B	C	D
	Yamayuri	A	A	A	A	A	A	A	A	D	D	D
	Xerox R	A	A	A	A	A	A	A	A	C	D	D

45 Claims

1. An ink for ink jet recording, comprising at least a water-soluble colorant, a water-soluble organic solvent, water, and a compound represented by the following formula (I), (II), or (III):

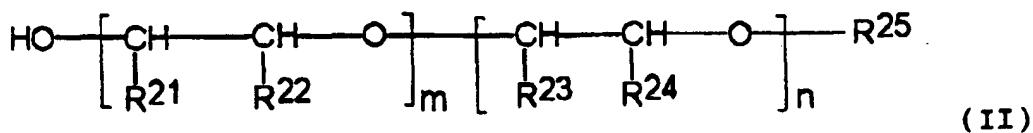
50

55



wherein

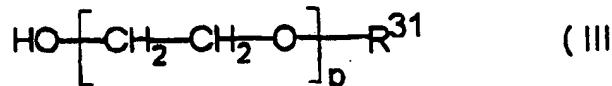
15 R^{11} , R^{12} , R^{13} , and R^{14} each independently represent a C_{1-6} alkyl group,
 A and B each independently represent a group consisting of an ethyleneoxy group and/or a propyleneoxy group, provided that any one of A and B contains at least one propyleneoxy group, and
 the total number of ethyleneoxy groups and propyleneoxy groups is 2 to 60;



30 wherein

any one of R^{21} and R^{22} represents H with the other substituent representing CH_3 or H, and any one of R^{23} and R^{24} represents H with the other substituent representing CH_3 or H,
 when any one of R^{21} and R^{22} represents H, both R^{23} and R^{24} represent H, and
 when both R^{21} and R^{22} represent H, at least one of R^{23} and R^{24} represents CH_3 ,
 R^{25} represents a C_{4-10} alkyl group, and
 m and n each are a number satisfying $2 \leq m + n \leq 6$;
 provided that the compounds wherein R^{21} , R^{22} , R^{23} , and R^{24} all represent H are excluded.

40 and



wherein R^{31} represents a C_{4-10} alkyl group and p is an integer of 3 to 6.

50 2. The ink according to claim 1, wherein the compound represented by the formula (I) has an HLB value of not less than 7.

3. The ink according to claim 1, wherein the amount of the compound represented by the formula (I) added is 0.1 to 10% by weight.

55 4. The ink according to claim 1, wherein the amount of the compound represented by the formula (II) added is 0.5 to 30% by weight.

5. The ink according to claim 1, wherein the amount of the compound represented by the formula (III) added is 3 to 30% by weight.
6. The ink according to claim 1, wherein the water-soluble colorant comprises a water-soluble dye and/or a water-soluble pigment dispersible in water.
- 5 7. The ink according to claim 6, which, when the water-soluble colorant is a water-soluble pigment, further comprises an emulsion.
- 10 8. The ink according to claim 7, wherein the amount of the emulsion added is 1 to 10% by weight.
9. The ink according to claim 7, wherein the emulsion has a core/shell structure comprising a core and a shell surrounding the core, the shell comprising a crosslinked resin.
- 15 10. An ink jet recording method comprising the step of ejecting a droplet of an ink composition and depositing the droplet onto a recording medium to perform printing, wherein the ink composition is one according to claim 1.
11. The method according to claim 10, wherein the droplet of the ink composition is ejected through a nozzle head having a water-repellent surface.
- 20 12. The method according to claim 11, wherein the water-repellent surface of the nozzle head is a surface having thereon an eutectoid plating of tetrafluoroethylene and a non-oxidizable metal.
13. The method according to claim 11, wherein the ink for ink jet recording has a contact angle of not less than 50° on the water-repellent surface of the nozzle head.
- 25 14. The method according to claim 10, wherein the droplet of the ink composition is ejected using an electrostrictive element and, when the ink composition is not ejected, the ink composition is slightly moved by the electrostrictive element to such an extent that the ink is not delivered from the nozzle.
- 30 15. The method according to claim 10, wherein the content of the water-soluble colorant in the ink composition is 3 to 15% by weight.
16. The method according to claim 10, wherein the ink composition is filled into an ink cartridge packed with a polyurethane foam.
- 35 17. A record produced by the method according to claim 10.

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DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages		
X	EP 0 594 081 A (CANON KK) 27 April 1994 * page 8, line 40 - line 56 * * page 9, line 27 * ---	1,4	C09D11/00 B41J2/045
X	EP 0 583 096 A (CANON KK) 16 February 1994 * page 6, line 33 - page 7, line 15; example 1 * ---	1,6	
A	* table 2 * ---	10	
A	EP 0 506 128 A (SEIKO EPSON CORP) 30 September 1992 * page 3, line 10 - page 4, line 20 * * page 4, line 21 - line 49 * ---	10,11	
A	EP 0 739 956 A (SONY CORP) 30 October 1996 * page 5, line 29 - line 34 * ---	10-17	
A	US 5 501 725 A (LAUW HIANG ET AL) 26 March 1996 * abstract * ---	16	
A	US 5 587 731 A (YASUNAGA KUNIaki ET AL) 24 December 1996 * the whole document * ---	16	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP 0 359 365 A (TEKTRONIX INC) 21 March 1990 * claims 1-3; examples 1-3 * ---	11-14	C09D B41J
A	US 5 563 640 A (SUZUKI MASAHIKO) 8 October 1996 * claims 1-14 * -----	10-14	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	26 August 1998	Miller, A	
CATEGORY OF CITED DOCUMENTS			
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